

Selective metal deposition for a structure with a thin intermediate layer on a photochromic diarylethene film

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Selective metal Mg deposition was achieved for a structure with the 8-nm-thick intermediate layer of Alq3 on a photochromic diarylethene (DAE) layer. Selective deposition for a structure with the Alq3 intermediate layer was attributed to uncolored DAE molecules exposed on the surface due to the migration and the aggregation of Alq3 molecules on the uncolored DAE layer. Laser spot irradiation enables both isomerization and an annealing effect on samples with an Alq3 intermediate layer, thereby achieving selective Mg deposition. Selective deposition for a structure with an intermediate layer could be important for the preparation of patterned cathodes in the field of organic electronics.

Introduction

Interest in the interfaces between metal layers and organic layers is growing as a result of the increasing use of organic materials in electronic devices. However, research in this area has mainly concentrated on problems associated with the injection of carriers into organic layers from metal electrodes.¹ The vacuum-evaporation method is widely used in preparing thin films, by which various metals or organic molecules are deposited on solid surfaces at room temperature.² Different from such well known phenomena, however, we found that the ability of some organic materials to accept metal atoms is dependent upon the state of the organic solid surface. Selective metal deposition means that metal vapor atoms are deposited selectively on a photochromic molecular surface depending on its isomerization state.³

Photochromism is defined as a reversible structural interconversion between two isomers upon irradiation by light at different wavelengths.⁴ Selective metal deposition occurs on photochromic diarylethene (1,2-bis[2-methyl-5-(5-trimethylsilylthien-2-yl)thien-3-yl]perfluorocyclopentene, DAE) film. On exposure to UV light, an uncolored state (DAEo) switches to the DAEc state, but reverts to the DAEo state on exposure to visible light. Magnesium metal vapor is deposited selectively on the DAE surface, depending on its state of photoisomerization; the metal vapor is deposited only on the colored state, as shown in Fig. 1. No metal Mg–Mg compounds have been determined on the uncolored film using X-ray photoelectron spectroscopy. No changes of hydrophobicity according to isomerization have been observed. Selective metal deposition on the photochromic molecular surface originates from a difference in the glass-transition temperature (T_g), or more precisely, in the activity of the surface molecular motion between the two states of the isomerization of amorphous DAE film.³ The T_g of amorphous DAE in the uncolored state is 32 °C, whereas it is 95 °C in the colored state. When the Mg atoms

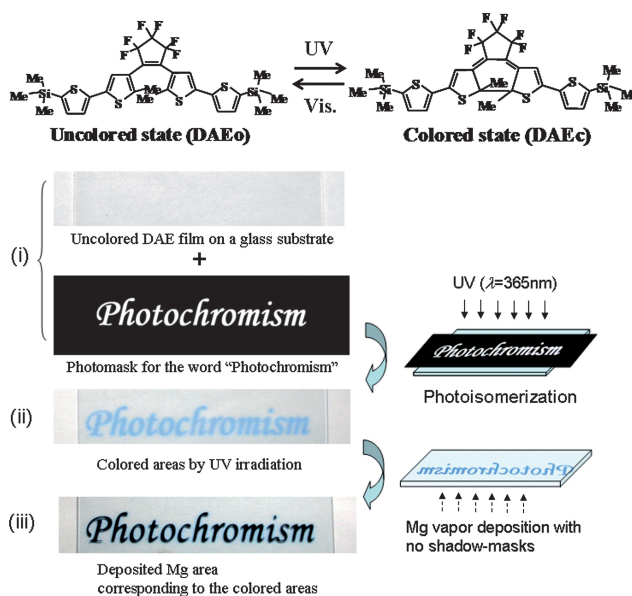


Fig. 1 Molecular structure change of photochromic diarylethene (DAE) and selective Mg deposition on a DAE film; (i) uncolored DAE film formed on glass substrate and a photomask; (ii) partially colored DAE film upon UV irradiation with the photomask; (iii) Mg films selectively deposited on colored areas.

are evaporated onto the uncolored DAE surface, weak van der Waals interactions and the active molecular motions of the DAE surface cause the active migration and rapid desorption of Mg atoms from the surface. Taking into account the strong correlation of selective deposition with T_g , the molecular motion is migration of the molecules on the film surface. Details about the origin and fundamentals of selective Mg deposition have been reported in ref. 3 and its supporting information.

Weak interaction and active migration will probably not be limited to cases of Mg atoms and the DAE surface. In this paper, we, therefore, report the influence of other materials on DAE surfaces with different isomerization states and discuss the possibility of selective deposition for a structure with a thin intermediate layer.

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Behavior of an organic molecule on a DAE layer

First, we investigated the possibility of deposition selectivity for tris(8-hydroxyquinolino)aluminum (Alq3), a widely used electron-transport material, on the photoisomerized DAE surface. Alq3 was evaporated onto the colored and uncolored DAE surface by an analogous process, shown in Fig. 1. As a result, selective deposition was not observed; Alq3 layers were formed on both surfaces. We did find, however, that the morphology of the Alq3 layer changed with the passage of time depending on the isomerization state of the DAE layer.

Fig. 2 shows the surface morphology changes in the samples with thin layers of Alq3 on the DAE surfaces. The samples had a 30-nm-thick DAE layer and an 8-nm-thick Alq3 intermediate layer and were prepared by different processes. In Sample 1, the Alq3 layer was deposited just after coloring the DAE layer by UV irradiation, whereas in Samples 2 and 3 the Alq3 layer was deposited on uncolored DAE layers. Sample 3 was colored by UV irradiation after the deposition of the Alq3 layer.

Atomic force microscopy (AFM) images were recorded on samples stored for 48 hours at 20 °C after Alq3 deposition. Small holes in the almost-uniform surface were observed in the Alq3 layer for Samples 1 and 3. In contrast, large holes and inhomogeneous unevenness were observed in the Alq3 layer in Sample 2. The areas surrounding these holes thickened, suggesting that movement and aggregation of Alq3 molecules had occurred on the uncolored surface. Although the states of DAE isomerization were different during Alq3 deposition in Sample 1 and 3, the AFM images of the resulting samples resembled each other. On the other hand, the AFM images of Samples 2 and 3 were quite different, despite the presence of the same isomerization states

during the Alq3-deposition stage. These results show that the surface change for Sample 2 occurred with the passage of time after Alq3 deposition; this change does not depend on the DAE state during Alq3 evaporation. This is a difference between Mg and Alq3 because the migration and desorption of the Mg atoms occurred during Mg evaporation.³

Magnesium deposition property on Alq3/DAE structure

The above result suggests the possibility of selective deposition for a structure with a thin Alq3 intermediate layer. Alq3 molecules on the uncolored DAE migrate, aggregate and form islands, and finally the uncolored DAE surface appears on the surface. On the other hand, the Alq3 layer does not change on the colored DAE surface. When Mg vapor is evaporated to the surface of the Alq3/DAE structure, we can expect that the Mg atoms will not be deposited on the uncolored state of DAE, but will be deposited on the colored state covered uniformly by Alq3.

To confirm the above expectation, we tested Mg deposition on annealed samples with Alq3/DAE structure. In general, since the above aging effects (obtained by the passage of time) are accelerated by high temperatures, we investigated the annealing/storage temperature dependence on the selective Mg deposition on samples with an Alq3 intermediate layer.

Fig. 3 shows the Mg deposition properties of the annealed/stored samples. The black area indicates deposited Mg. The samples have an 8-nm-thick Alq3 layer deposited on the colored or uncolored 30-nm-thick DAE films, which were stored at 0, 30 or 50 °C. Mg was deposited on the surfaces of all the colored

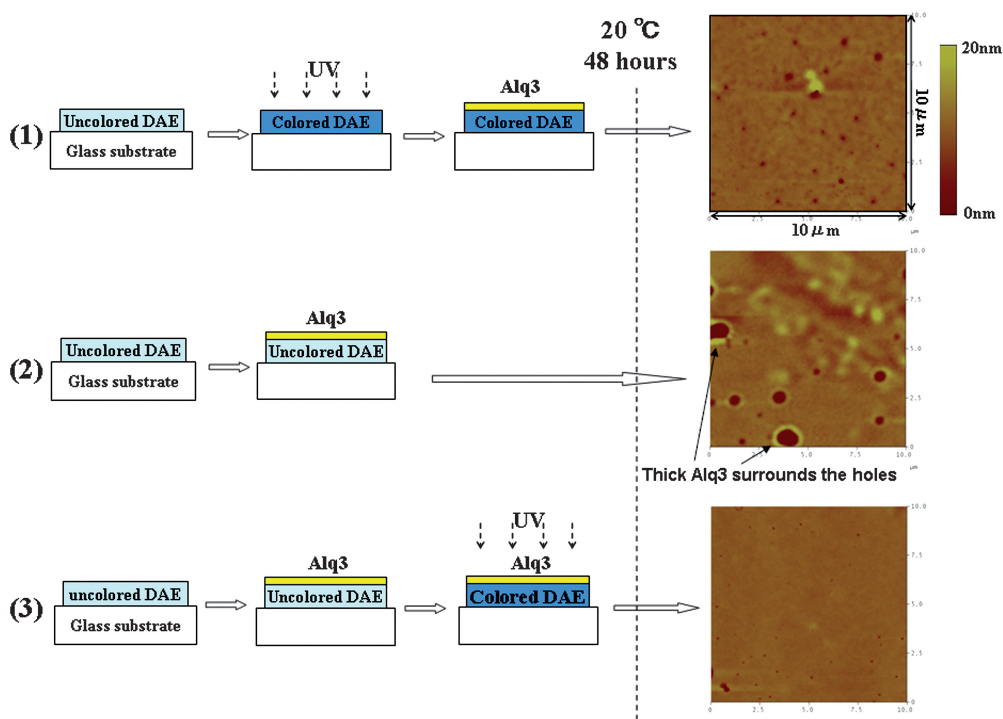


Fig. 2 Process dependence for surface morphology change of thin Alq3 layers on DAE layers. The thickness of Alq3 and DAE layers was 8 and 30 nm, respectively.

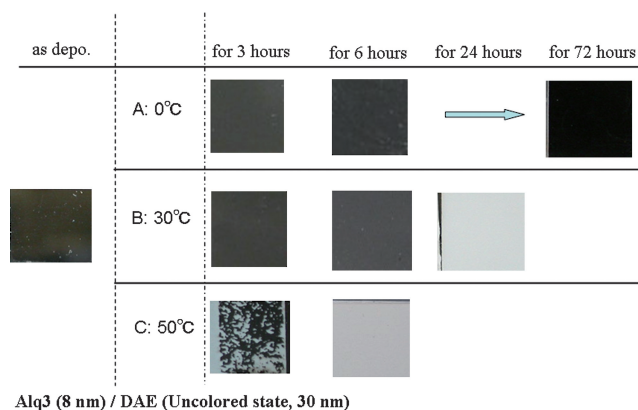


Fig. 3 Annealing condition dependence of Mg deposition for samples with Alq3 intermediate layer. Black areas correspond to deposited Mg films.

samples. Mg was also deposited on the uncolored sample just after Alq3 evaporation (denoted “as depo.” in Fig. 3), meaning the thin Alq3 layer uniformly covered the uncolored DAE layer and DAE did not appear on the surface. Furthermore, Mg was deposited on the uncolored sample stored at 0 °C for 72 hours, as shown in Fig. 3A, indicating that no change in uniform Alq3 layer occurred. On the other hand, Mg was deposited on the uncolored sample annealed at 30 °C for 3 hours, but not on the sample for 24 hours (Fig. 3B). The sample annealed at 50 °C for 3 hours showed uneven deposition of Mg. These results show that the undeposition effect is achieved by annealing at high temperatures, even for structures with an intermediate layer.

The occurrence of selective deposition on structures with an intermediate layer suggests the existence of uncolored DAE molecules on the surface as a result of changes in the intermediate layer. Fig. 4 shows the results of time-of-flight selective-ion mass spectroscopy (ToF-SIMS) studies of the surface with an 8-nm-thick intermediate layer of Alq3 on the uncolored DAE layer after storage at 30 °C for 24 hours. The ToF-SIMS

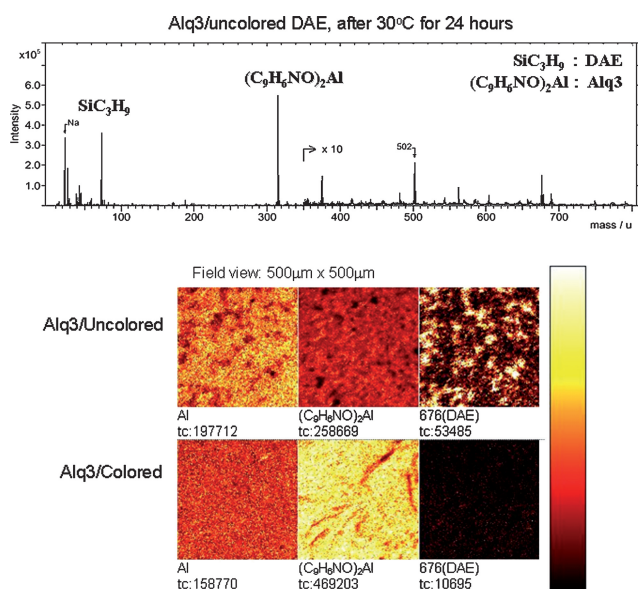


Fig. 4 ToF-SIMS characterization for annealed sample with Alq3 intermediate layer on the uncolored DAE surface.

characterization determines which species of molecular fragments are present within 1 nm from the surface. The observation of the fragment SiC_3H_9 in the upper figure shows the existence of DAE on the surface. The lower images in Fig. 4 also compare the surface of the Alq3/colored DAE and Alq3/uncolored DAE samples. No DAE molecules were observed on the surface on the Alq3/colored DAE sample, whereas non-uniform distribution of DAE was confirmed on the Alq3/uncolored DAE sample. This is clear evidence that the existence of uncolored DAE is caused by a change in the Alq3 layer.

Selective metal deposition using laser spot irradiation

Based on the above results, we investigated whether selective metal deposition upon laser irradiation is possible for a device with an intermediate layer of Alq3, as laser scanning is a promising method for obtaining fine metal electrode/wiring using mask-less vacuum evaporation.

Since irradiation by laser light can produce an annealing effect as well as photoisomerization, we examined selective deposition by the process shown in Fig. 5. DAE and intermediate layers were deposited sequentially on a glass substrate by a vacuum-evaporation method. The DAE layer on the glass substrate was colored by UV irradiation just after deposition, and then a thin Alq3 layer was formed. DAE and intermediate layers of various thicknesses were produced. The samples were then irradiated with a red laser spot with a 630 nm wavelength, a 1 mm diameter, and 3 mW laser to decolorize the central area. Finally, Mg was evaporated onto the samples without evaporation masks at a deposition rate of 0.5–2.0 nm s^{-1} to give a Mg layer with a thickness of 20 to 50 nm.

Fig. 6 shows the result of selective Mg deposition by laser irradiation for the Alq3 intermediate layer structure. The left-hand upper image “Y” shows the occurrence of selective deposition; that is, Mg films were not formed on the uncolored central spot area; the left-hand lower image “N” shows the absence of selective deposition. The right-hand image summarizes the thickness dependence of selective deposition for the Alq3/DAE structure. Selective deposition occurs for structures with an intermediate layer less than 10 nm thick, which is thinner than the DAE layer.

Fig. 7 shows the AFM images of the uncolored spot area generated by laser irradiation corresponding to (A) and of the colored area corresponding to (B) in the left-hand upper image of Fig. 6. Images (a-1) and (b-1) correspond to areas (A) and (B) before Mg deposition, respectively. Image (a-1) shows a large island growth of Alq3 on the uncolored DAE film. On the other hand, a mesh structure was observed on the colored DAE in image (b-1). It is well known that the development of mesh or island structures takes place at the beginning of a film growth

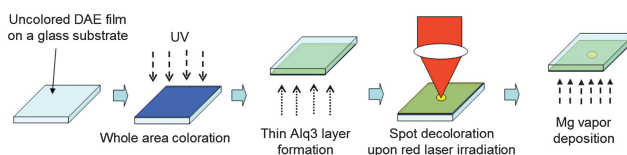


Fig. 5 Laser irradiation process for the samples with Alq3 intermediate layer on colored DAE layer.

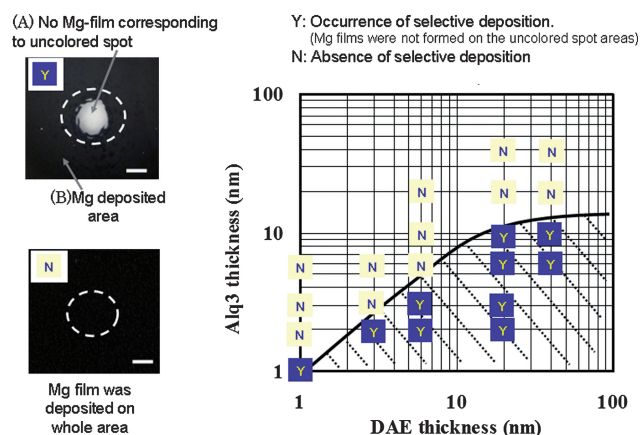


Fig. 6 Selective Mg deposition using laser irradiation for samples with Alq3 intermediate layer. Left-hand images indicate outlooks of Mg deposition and right-hand image shows thickness dependence of selective deposition. “Y” shows the occurrence of selective deposition, that is, Mg atoms were not deposited on the uncolored center spot area, and “N” shows absence of selective deposition. Dotted line area indicates the zone where the selective deposition is produced. Scale bars in the left-hand image represent 0.5 mm.

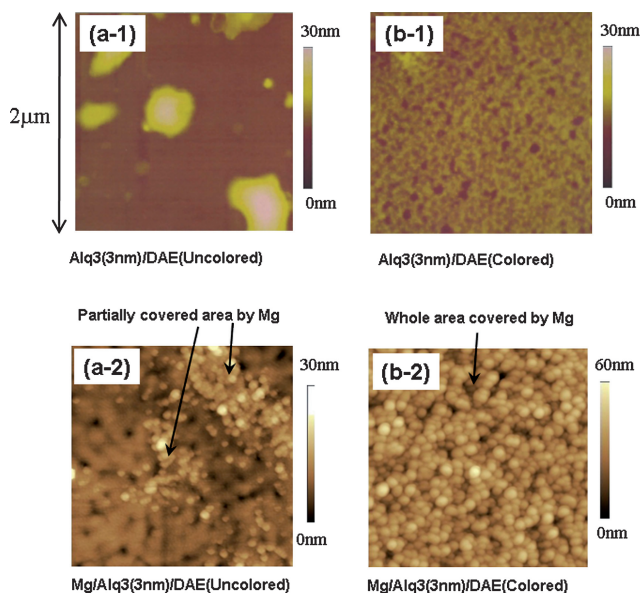


Fig. 7 AFM images for the samples with uncolored spot area generated by laser irradiation. (a-1) and (b-1) correspond to uncolored and colored areas before Mg deposition, respectively. (a-2) and (b-2) also show corresponding areas to (a-1) and (b-1) after Mg deposition, respectively.

process and that the effective growth of islands results in the active migration of molecules on the surface.² These observations, therefore, indicate that the deposited Alq3 molecules move more easily on the uncolored DAE surface than on the colored DAE and migrate to form island structures in the former. This suggests the existence of DAE molecules on the surface in the area other than the Alq3 islands in image (a-1). Fig. 7 (a-2) and (b-2) also show the AFM images of the samples corresponding to (a-1) and (b-1) after Mg evaporation, respectively. Mg crystals cover the whole surface in (b-2), whereas the areas that consisted of Mg crystals on Alq3 islands were observed in (a-2). This is

because Mg vapor atoms were only deposited on the Alq3 surface and not on the uncolored DAE surface. It showed no deposition of Mg for the annealed Alq3/DAE sample in Fig. 3 and the laser irradiated area in Fig. 6. The islands that Mg was deposited on are quite small Alq3 areas on the surface, and therefore, it seems not to exist. AFM image (a-2) in Fig. 7 indicates the existence of such small Mg deposited areas on the surface.

Fig. 8 illustrates a model of the change in the thin Alq3 layer on the uncolored DAE layer. The thin Alq3 film is homogeneous on the colored and uncolored DAE surfaces just after deposition. As a consequence of annealing by laser irradiation, Alq3 molecules migrate on the uncolored DAE surface, causing changes in the Alq3 layer, and finally aggregate to form islands of Alq3. The change in the Alq3 film is attributed to the effect of the low T_g of the uncolored DAE, as well as annealing. When the temperature is around or higher than T_g , DAE molecules are in a state of active molecular motion. As a result, Alq3 molecules on the uncolored DAE layer are affected by the active molecular motion of DAE; they move around on the DAE surface and finally aggregate to islands. Consequently, uncolored DAE is exposed on the surface, and the undeposition effect becomes effective. Mg atoms are deposited only on Alq3 islands. On the other hand, the Alq3 layer on the colored surface does not change. This model also explains why thick Alq3 areas surround the holes in the AFM image of Sample 2 in Fig. 2. When the intermediate layer is thick, retention of the film itself becomes more pronounced and no changes occur. This is the mechanism of selective deposition in the structure with the intermediate layer.

Selective deposition was also observed for structures with an intermediate layer composed of *N,N*-di(1-naphthyl)-*N',N'*-diphenylbiphenyl-4,4'-diamine (NPB, a typical hole-transport

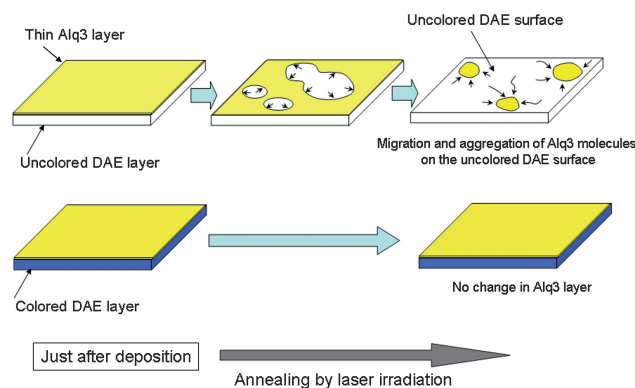


Fig. 8 Model for laser annealing effect for Alq3 intermediate layer on DAE surface.

Table 1 Selective Mg deposition for the NPB, Ag or Al intermediate layer sample. (DAE thickness: 25 nm). Labels “Y” and “N” denote the occurrence (Mg films were not formed on the uncolored spot areas.) and absence of the selective deposition, respectively

Thickness of an intermediate layer /nm	0	4	6	8	10	20
NPB	Y	Y	Y	Y	N	N
Ag	Y	Y	Y	Y	N	N
Al	Y	Y	Y	Y	N	N

organic material), Ag or Al. Table 1 shows the results for NPB, Ag or Al intermediate layers; similar thickness dependencies to Alq3 for the 25-nm-thick DAE layer were observed.

Discussion of applications

The selective deposition technique has considerable potential for use in the field of organic electronics. Mg is a widely used electrode material for organic devices due to its low work function for electron injection into an organic layer.⁵ Selective deposition should enable the production of fine metal electrodes without evaporation masks, simply by scanning with a laser light spot. Metal species would not be restricted to Mg; the potential for using Al or Ca has been discussed.³

In general, however, a metal cathode is deposited directly on an electron transport/injection layer, and the existence of the DAE layer for selective deposition may block electron injection. In such a case, the selective deposition effect for a structure with an intermediate layer reported here would resolve that problem. In this paper, we mainly investigated selective deposition for a structure with an Alq3 intermediate layer, but selective deposition for a variety of intermediate layers, containing other organic or metal layers, has also been achieved. Many kinds of carrier injection layers have been reported in organic electronics.⁶ The selective deposition method for a structure with an intermediate layer would be applicable to such intermediate layers for improving carrier injection.⁷

Conclusions

We successfully demonstrated selective Mg deposition for a structure with a thin intermediate layer on the DAE film. Selective deposition was achieved for a sample with an 8-nm-thick intermediate layer of Alq3 between layers of DAE and Mg after annealing treatment. The origin of selective deposition for the structure with the Alq3 intermediate layer was that uncolored DAE molecules were present on the surface due to the migration and the aggregation of the Alq3 molecules on the uncolored DAE layer. Laser irradiation causes both isomerization and an annealing effect on samples with an Alq3 intermediate layer, thereby achieving selective Mg deposition. The selective deposition method could be an important technique for the preparation of patterned cathodes in the field of organic electronics.

Experimental

Glass substrates were pre-cleaned by ultrasonic treatment in acetone and by a UV-ozone cleaner. Organic materials including DAEs and metals were deposited on the substrate using a conventional vacuum-evaporation method. All evaporation

experiments were carried out at room temperature under pressure conditions below 6×10^{-4} Pa. Film thickness was controlled using a quartz thin film monitor during evaporation and directly measured using a monochromatic light interference method. The thicknesses of the thin films were estimated from the measurements of the quartz thickness monitor. Mg films were prepared with a deposition rate of 0.5–2.0 nm s⁻¹. The deposited Mg thickness was set at 20–100 nm.

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